Pergamon

PII: S0277-5387(97)00011-9

Polyhedron Vol. 16, No. 16, pp. 2843–2850, 1997

0277-5387/97 \$17.00+0.00

Crystal structures of chloro(*meso*-tetraphenylporphyrinato)germanium(IV), Ge(tpp)Cl_2, and dihydroxo(*meso*-tetraphenylporphyrinato)germanium(IV), Ge(tpp)$(OH)_2$, and two-stage hydrolysis of its homologue dimethoxo(*meso*-tetraphenylporphyrinato)germanium(IV), Ge(tpp)$(OMe)_2$

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(Received 30 September 1996; accepted 12 December 1996)

Abstract—The crystal structures of chloro(*meso*-tetraphenylporphyrinato)germanium(IV), Ge(tpp)Cl_2, dimethoxo(*meso*-tetraphenylporphyrinato)germanium(IV), Ge(tpp)$(OMe)_2$, and dihydroxo(*meso*-tetraphenylporphyrinato)germanium(IV), Ge(tpp)$(OH)_2$, were determined. The coordination sphere of the Ge^{4+} ion is a distorted octahedron in which the apical sites are occupied by two monodentate Cl^- (or OMe^-, OH^-) groups. The geometry around the germanium centre of the Ge(tpp)Cl_2 molecule has Ge(1)—Cl(1) = 2.262(1) and Ge(1)—N(1) = 2.019(2) Å. In the structure of Ge(tpp)$(OMe)_2$ the germanium(1)–oxygen distance is 1.826(3), average Ge(1)—N = 2.032(3), and O(1)—C(23) = 1.331(6) Å. The structure of Ge(tpp)$(OH)_2$ has Ge(1)—O(1) = 1.809(3) and Ge(1)—N(1) = 2.027(2) Å. Two-stage hydrolysis of Ge(tpp)$(OMe)_2$ was studied by ^1H and ^{13}C NMR spectroscopy. The use of a limited amount of water in $CDCl_3$ (or CD_2Cl_2) allowed the hydrolysis intermediate, hydroxomethoxo(*meso*-tetraphenylporphyrinato)germanium(IV), Ge(tpp)(OMe)(OH), and hydrolysis product, dihydroxo(*meso*-tetraphenylporphyrinato)germanium(IV), Ge(tpp)$(OH)_2$, to be identified. X-ray diffraction data and solid-state ^{13}C CP/MAS spectra of Ge(tpp)$(OMe)_2$ provide evidence for two monodentate methoxo groups coordinated to the germanium(IV) atom. © 1997 Elsevier Science Ltd

Keywords: crystal structure; germanium porphyrins; ^{13}C CP/MAS; two-stage hydrolysis; monodentate ligand; *trans* geometries.

Kenney and coworkers [1] first reported the synthesis and ^1H NMR characterization of dichloro(*meso*-tetraphenylporphyrinato)germanium(IV), Ge(tpp)Cl_2, and dihydroxo(*meso*-tetraphenylporphyrinato)germanium(IV), Ge(tpp)$(OH)_2$. The structures of the dimethoxyporphyrinatogermanium(IV), Ge(p)$(OMe)_2$ [2], difluoro(octaethylporphyrinato)germanium(IV), Ge(oep)F_2 [3], Ge(tpp)$(OOCH_2CH_3)_2$ [4], and Ge(tpp)$(OCH_2CH_3)_2$ [4], have been published. As Ge(tpp)Cl_2 (**1**) and Ge(tpp)$(OH)_2$ (**4**) are the starting materials for the preparation of these Ge^{IV} tpp

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di(alkoxy) and difluoro complexes, it is important to determine their structures precisely. Details of the synthetic work were reported elsewhere [1]. We report here the structures of Ge(tpp)Cl_2 (**1**) and Ge(tpp)$(OH)_2$ (**4**) derived from ^{13}C NMR and X-ray diffraction. Meanwhile, Ge(p)$(OMe)_2$ was found to be hydrolytically unstable [2]. When the porphyrin group of Ge(p)$(OMe)_2$ was substituted by tetraphenylporphyrin, Ge(p)$(OMe)_2$ became dimethoxo(*meso*-tetraphenylporphyrinato) germanium(IV) Ge(tpp)$(OMe)_2$ (**2**). Previously, we reported the two-stage (or two-step) hydrolysis of dimethoxo(*meso*-tetraphenylporphyrinato)tin(IV), Sn(tpp)$(OMe)_2$ [5], and dimethoxo(tetra-p-tolyporphyrinato)tin(IV), Sn(tptp)$(OMe)_2$ [6]. It led us to think that complex Ge(tpp)$(OMe)_2$, the same Group 14 metals as Sn(tpp)$(OMe)_2$, might undergo a similar two-stage hydrolysis reaction in the presence of water. Compound **2** was easily prepared by the previously reported method [2] and its X-ray structure and solid-state ^{13}C CP/MAS data are reported here.

EXPERIMENTAL

Syntheses

Ge(tpp)Cl_2 (**1**). Compound **1** was prepared as previously reported [1], except that the resultant purple crystalline compound was recrystallized from $CHCl_3$/*n*-hexane and vacuum dried. The crystals were grown by diffusion of ether vapor into a $CHCl_3$ solution. It was dissolved in $CDCl_3$ (99.8% from CIL) for ^1H (Table 1) and ^{13}C (Table 2) NMR measurement at 24°C.

Ge(tpp)$(OH)_2$ (**4**). Ge(tpp)Cl_2 (**1**. 99 mg, 0.13 mmol) in $CHCl_3$ was treated with Al_2O_3 (3 g, neutral, activity V) and stirred for 30 min. After concentrating, it was passed down a column of alumina (25 g, neutral, activity V). The major red band eluting with $CHCl_3$ was collected and concentrated and then recrystallized from $CHCl_3$/*n*-hexane. It gave Ge(tpp)$(OH)_2$ (78 mg, 84%). The crystals were grown by diffusion of *n*-hexane vapor into a $CHCl_3$ solution. Ge(tpp)$(OH)_2$ (**4**) was dissolved in $CDCl_3$ (or CD_2Cl_2) for NMR measurement at 24°C (shown in Tables 1 and 2).

Ge(tpp)$(OMe)_2$ (**2**). The crystals of compound **2** were obtained by allowing methanol to diffuse into a nearly saturated solution of Ge(tpp)$(OH)_2$ in $CHCl_3$. It was dissolved in $CDCl_3$ (or CD_2Cl_2) for NMR measurement at 24°C (shown in Tables 1 and 2).

Spectroscopy

^1H and ^{13}C NMR spectra were recorded at 400.13 (or 600.20) and 100.61 (or 150.93) MHz, respectively, on a Bruker AM-400 spectrometer (or Bruker DMX-600) in $CDCl_3$ or CD_2Cl_2. ^{13}C NMR data are relative to the centerline of $CDCl_3$ at 77.0 ppm (or CD_2Cl_2 at 53.6 ppm). The solid-state ^{13}C CP/MAS MSL-200 solid-state NMR spectrometer. Dry nitrogen gas was used to drive MAS rates of 3.2 KHz.

Crystallography

Crystal data and other information for Ge(tpp)Cl_2 (**1**), Ge(tpp)$(OMe)_2$ (**2**) and Ge(tpp)$(OH)_2$ (**4**) are given in Table 3. Measurements were made on a Siemens SMART CCD diffractometer using monochromatized Mo-$K\alpha$ radiation ($\lambda = 0.71073$ Å) *via* the $\omega : 2\theta$ scan technique. Absorption corrections were

Table 1. Proton chemical shift (δ) for compounds **1**–**4** and MeOH in $CDCl_3$ at 24°C[a]

Compounds	β-H	*o*-H	*m*, *p*-H	OMe	OH
Ge(tpp)$(OMe)_2$ (**2**)	9.02	8.28 (m)[b]	7.79 (m)	−2.57	—
Ge(tpp)(OMe)(OH) (**3**)	9.04	8.28 (m)	7.79 (m)	−2.59	−6.99[d] (−6.73)[e]
Ge(tpp)$(OH)_2$ (**4**)	9.03	8.26 (8 Hz)[c]	7.77 (7 Hz)	—	−6.99[d] (−6.70)[e]
MeOH	—	—	—	3.34	—
Ge(tpp)Cl_2 (**1**)	9.10	8.24 (m)	7.79 (m)	—	—

[a] Chemical shifts in ppm relative to $CDCl_3$ at 7.24 ppm.

[b] m = multiplet.

[c] ^3J(H—H) coupling constants in Hz.

[d] Broad singlet.

[e] Measured in CD_2Cl_2 at −80°C and chemical shifts are given in ppm relative to CD_2Cl_2 at 5.30 ppm.

Table 2. ^{13}C Chemical shift (δ) of compounds **1**–**4** and MeOH in $CDCl_3$ at 24°C at 100.61 MHz and ^{13}C CP/MAS for compound **2**[a]

Medium and compound (carbon frequency)	C_α	C_1	$C_{2,6}$	C_β	C_4	$C_{3,5}$	C_m	OMe
$Ge(tpp)(OMe)_2$ (**2**) ^{13}C CP/MAS (solid) (50.33 MHz)	146.5	140.2	132.3		128.1		120.9	47.4
$Ge(tpp)(OMe)_2$ (**2**) solution	146.1 (146.4)[b]	—	134.6	131.1 (131.2)[b]	128.1	126.9	— (120.2)[b]	—
Ge(tpp)(OMe)(OH) (**3**) solution	145.8 (146.0)[b]	141.2	134.7	131.2 (131.3)[b]	128.1	126.9	119.5 (120.0)[b]	43.7
$Ge(tpp)(OH)_2$ (**4**) solution	145.5 (145.6)[b]	141.3	134.7	131.4 (131.4)[b]	128.1	126.9	119.3 (119.7)[b]	—
MeOH	—	—	—	—	—	—	—	50.7
$Ge(tpp)Cl_2$ (**1**) solution	144.9	140.1	134.5	131.3	128.5	127.2	118.8	—

[a] Chemical shifts in ppm relative to the centerline of $CDCl_3$ at 77.0 ppm.

[b] They were measured in CD_2Cl_2 at 24°C and chemical shifts were in ppm relative to the centerline of CD_2Cl_2 at 53.6 ppm.

Table 3. Crystal data for compounds $Ge(tpp)Cl_2$ (**1**), $Ge(tpp)(OMe)_2$ (**2**) and $Ge(tpp)(OH)_2$ (**4**)

Formula	$C_{44}H_{28}Cl_2GeN_4$ (**1**)	$C_{46}H_{34}GeN_4O_2$ (**2**)	$C_{44}H_{30}GeN_4O_2$ (**4**)
Formula weight	756.2	747.4	719.3
a (Å)	13.5872(5)	19.4130(2)	13.3943(4)
b (Å)	—	—	13.3942(3)
c (Å)	9.9293(5)	9.7952(1)	9.7255(1)
V (Å^3)	1833.1(5)	3691.5(9)	1744.8(1)
Z	2	4	2
D_c (g cm^{-3})	1.370	1.345	1.369
Space group	$I4$	$P4_2/n$	$I4/m$
F(000)	772	1544	740
μ (cm^{-1})	10.19	8.75	9.23
R^a (%)	2.84	4.51	2.83
$R_w{}^b$ (%)	3.42	6.17	3.46
GOF	1.11	1.01	1.82
A^b	1	1	1
B^b	4×10^{-4}	3.1×10^{-3}	6×10^{-4}
Crystal size (mm^3)	$0.31 \times 0.30 \times 0.29$	$0.62 \times 0.50 \times 0.30$	$0.175 \times 0.375 \times 0.625$
Data collected	4483	10483	3999
$2\theta_{max}$ (°)	51.1	51.1	50.9
Temperature (K)	296	296	296
Data used	1441	2094	795
Discrimination	$I \geqslant 3.0\sigma(I)$	$I \geqslant 3.0\sigma(I)$	$I \geqslant 3.0\sigma(I)$

[a] $[\Sigma \| F_o | - | F_c \| / \Sigma F_o |]$.

[b] $R_w = [\Sigma w(\| F_o | - | F_c \|)^2 / \Sigma w(|_o|)^2]^{1/2}$; $w = A/(\sigma^2 F_O + BF_O^2)$.

based on 4614 (or 3314, 3608) symmetry-equivalent reflections using the SHELXTL-PC program package with [$T_{min,max} = 0.780, 0.920$ or $T_{min,max} = 0.836, 0.964$ or $T_{min,max} = 0.753, 0.950$)] for compound **1** (or **2** or **4**), respectively. The structures were solved by direct methods (SHELXTL PLUS) and refined by full-matrix least-squares. All non-hydrogen atoms were refined with anisotropic thermal parameters, whereas all hydrogen-atom positions were located on a difference map and included in the structure-factor calculation. Selected bond distances and angles for compounds **1**, **2** and **4** are given in Table 4.

RESULTS AND DISCUSSION

Molecular structures of $Ge(tpp)Cl_2$ (**1**), $Ge(tpp)(OMe)_2$ (**2**) *and* $Ge(tpp)(OH)_2$ (**4**)

The skeletal framework of the complexes $Ge(tpp)Cl_2$ (**1**), with $I\bar{4}$ symmetry [or $Ge(tpp)(OMe)_2$ (**2**) with $P4_2/n$, $Ge(tpp)(OH)_2$ (**4**) with $I4/m$ symmetry] are illustrated in Figs 1(a), (b) and (c). They reveal the six-coordination of the germanium atom (Ge) with four nitrogen atoms of the porphyrinato group and two Cl^- (or the two OMe^-, two OH^-) for compound **1** (or compounds **2** and **4**), respectively. Bond distances are Ge(1)—Cl(1) = 2.262(1) and Ge(1)—N(1) = 2.019(2) Å for compound **1**, Ge(1)—O(1) = 1.826(3), Ge(1)—N(1) = 2.022(3), Ge(1)—N(2) = 2.041(3), O(1)—C(23) = 1.331(6) Å for compound **2** and Ge(1)—O(1) = 1.809(3), Ge(1)—N(1) = 2.027(2) Å for compound **4**. The geometry about the Ge is a distorted octahedron. The dihedral angles between the mean plane of the skeleton ($C_{20}N_4$) and the planes of the phenyl group are 89.2° [C(9)] for compound **1**, 70.3 [C(14)], 69.5° [C(20)] for compound **2** and 90.0° [C(9)] for compound **4**. The Ge atom lies on the geometrical center C_t') of the mean plane of the 24-atom core. The radii of the central "hole" ($C_t' \cdots N$, distance from the C_t' to the porphyrinato-core N atoms) are 2.019 Å for compound **1**, 2.032 Å for compound **2** and 2.027 Å for compound **4**. These distances are slightly larger than 2.01 Å suggested by Collins *et al.* [7]. Hence, the Ge^{IV} atom is bonded and centered in a slightly expanded porphyrinato core ($C_{20}N_4$) in compounds **1**, **2** and **4**. The same space group, $I4/m$, for compound **4** and the tin analog of **4**, $Sn(tpp)(OH)_2$, indicate that they are isostructural [8]. The radius of the central hole of 2.027 (or 2.019 Å) for **4** (or **1**) is shorter than 2.106 Å (or 2.098 Å) in $Sn(tpp)(OH)_2$ [or $Sn(tpp)Cl_2$] [8, 9].

Two-stage hydrolysis of $Ge(tpp)(OMe)_2$ (**2**)

$Ge(tpp)(OMe)_2$ (**2**) is sensitive to hydrolysis. When water is present in a $CDCl_3$ (or CD_2Cl_2) solution of $Ge(tpp)(OMe)_2$, resonances due to $Ge(tpp)(OMe)(OH)$ (**3**) and $Ge(tpp)(OH)_2$ (**4**) develop. The hydrolysis of $Ge(tpp)(OMe)_2$ (**2**) may be understood in terms of two-stage equilibrium reactions.

$$\underset{\mathbf{(2)}}{\mathrm{Ge(tpp)(OMe)_2}} + \mathrm{H_2O} \overset{K_1}{\rightleftharpoons} \underset{\mathbf{(3)}}{\mathrm{Ge(tpp)(OMe)(OH)}} + \mathrm{MeOH} \quad \text{(stage 1)}$$

$$\underset{\mathbf{(3)}}{\mathrm{Ge(tpp)(OMe)(OH)}} + \mathrm{H_2O} \overset{K_2}{\rightleftharpoons} \underset{\mathbf{(4)}}{\mathrm{Ge(tpp)(OH)_2}} + \mathrm{MeOH} \quad \text{(stage 2)}$$

where K_1 and K_2 are the equilibrium constants for stages 1 and 2. The ^{13}C NMR spectrum from the hydrolysis of $Ge(tpp)(OMe)_2$ (**2**) in $CDCl_3$ at reaction

Table 4. Selected bond distances (Å) and bond angles (°) for compounds **1**, **2** and **4**

Compound 1			
Ge(1)—Cl(1)	2.262(1)	Ge(1)—N(1)	2.019(2)
Cl(1)—Ge(1)—Cl(1a)	180.0(1)	N(1)—Ge(1)—N(1a)	179.5(5)
Cl(1)—Ge(1)—N(1)	90.2(2)	N(1)—Ge(1)—N(1b)	90.0(1)
Cl(1a)—Ge(1)—N(1a)	89.8(2)		
Compound 2			
Ge(1)—O(1)	1.826(3)	O(1)—C(23)	1.331(6)
Ge(1)—N(1)	2.022(3)	Ge(1)—N(2)	2.041(3)
C(23)—O(1)—Ge(1)	125.4(3)	O(1)—Ge(1)—N(1)	93.4(1)
O(1)—Ge(1)—O(1a)	180.0(1)	O(1)—Ge(1)—N(2)	87.9(1)
N(1)—Ge(1)—N(2)	90.2(1)	O(1)—Ge(1)—N(1a)	86.6(1)
N(1)—Ge(1)—N(1a)	180.0(1)	O(1)—Ge(1)—N(2a)	92.1(1)
N(1)—Ge(1)—N(2a)	89.8(1)	O(1a)—Ge(1)—N(1)	86.6(1)
N(2)—Ge(1)—N(1a)	89.8(1)	O(1a)—Ge(1)—N(2)	92.1(1)
N(2)—Ge(1)—N(2a)	180.0(1)	O(1a)—Ge(1)—N(1a)	93.4(1)
N(1a)—Ge(1)—N(2a)	90.2(1)	O(1a)—Ge(1)—N(2a)	87.9(1)
Compound 4			
Ge(1)—O(1)	1.809(3)	Ge(1)—N(1)	2.027(2)
O(1)—Ge(1)—O(1a)	180.0(1)	N(1)—Ge(1)—N(1a)	180.0(1)
O(1)—Ge(1)—N(1)	90.0(1)	N(1)—Ge(1)—N(1b)	90.0(1)

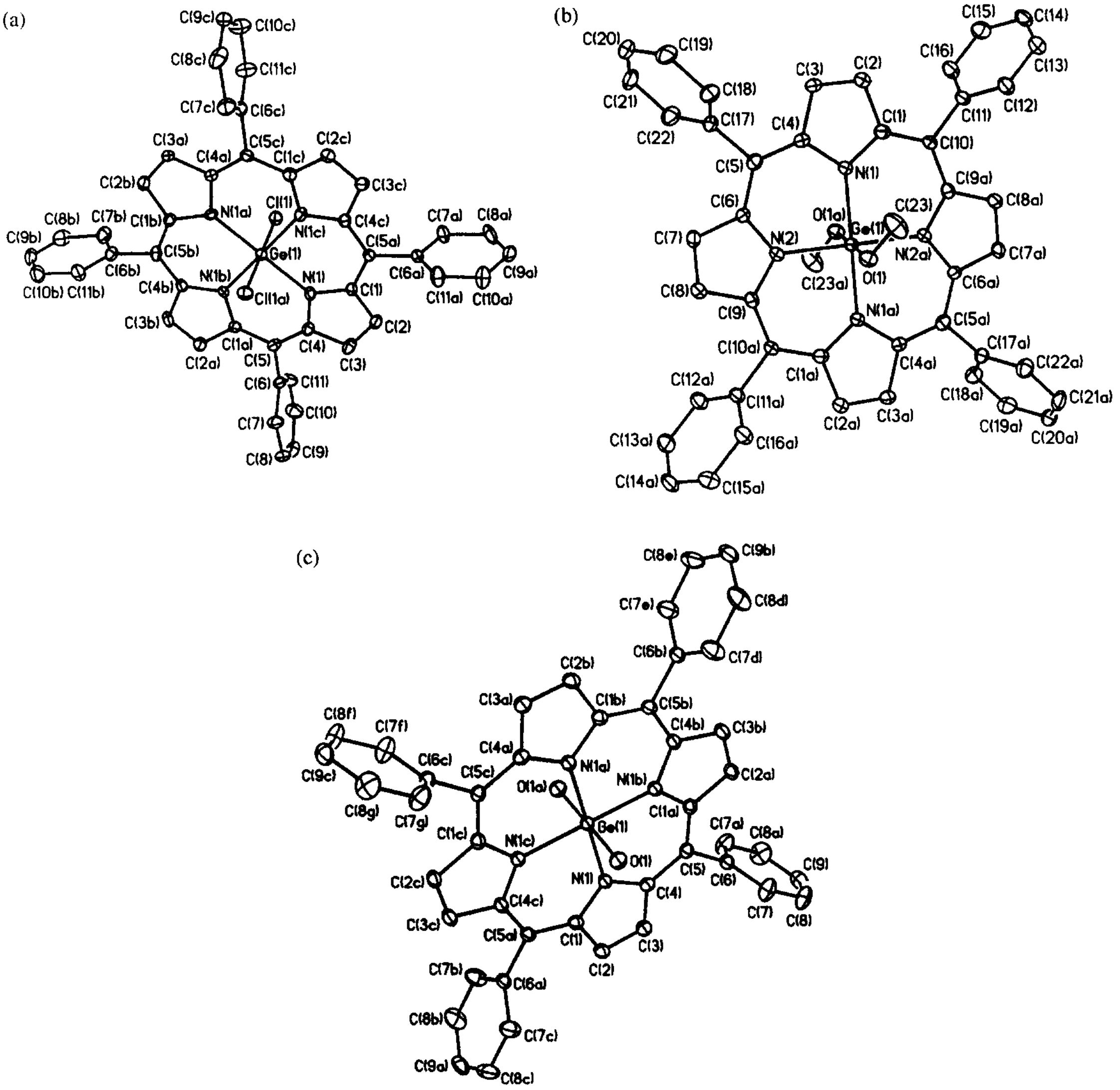


Fig. 1. Molecular configurations and atoms labeling schemes for (a) Ge(tpp)Cl_2 (**1**), (b) Ge(tpp)$(OMe)_2$ (**2**) and (c) Ge(tpp)$(OH)_2$ (**4**). Hydrogen atoms are omitted for clarity.

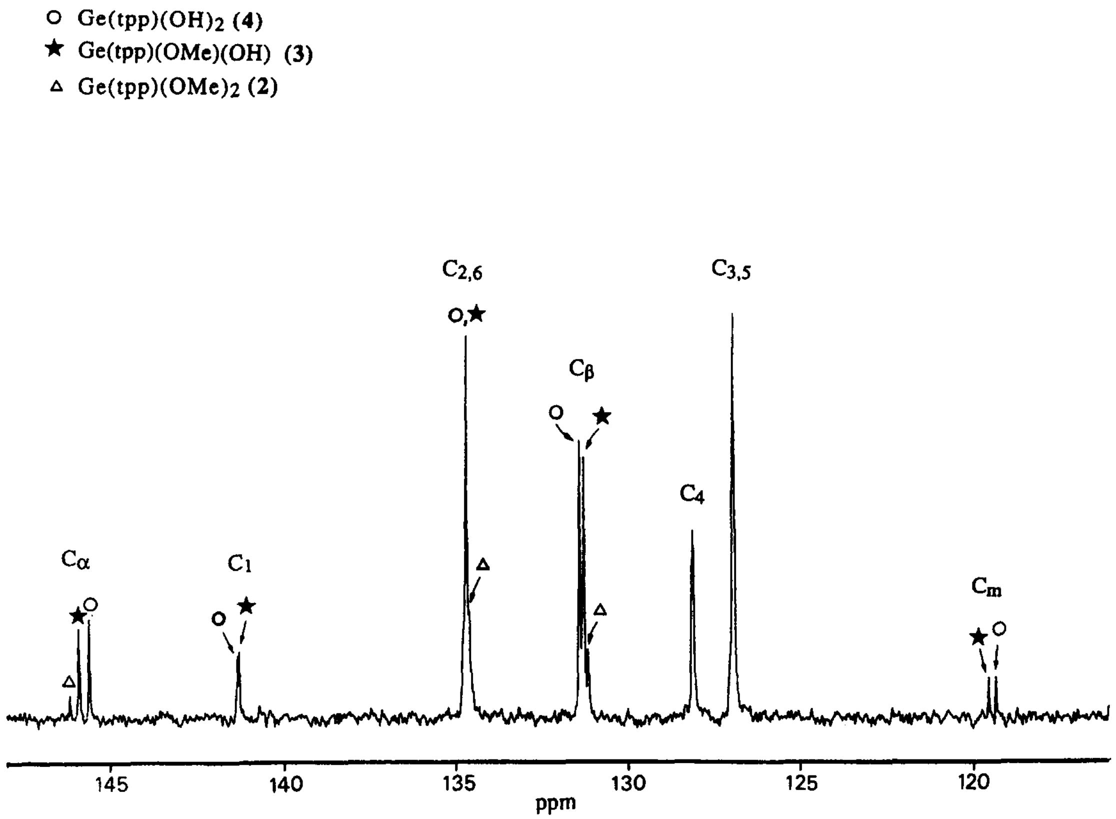
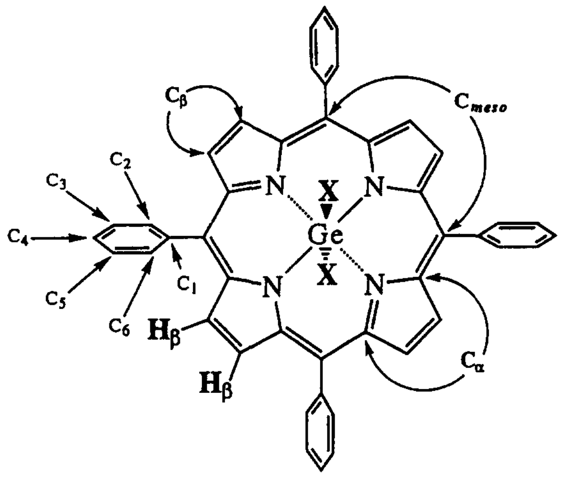


Fig. 2. The 100.61 MHz ^{13}C broad band NMR spectrum for Ge(tpp)(OMe)$_2$ (2) hydrolysis in CDCl$_3$ at 24°C after reaction time of several minutes.



where X = OMe

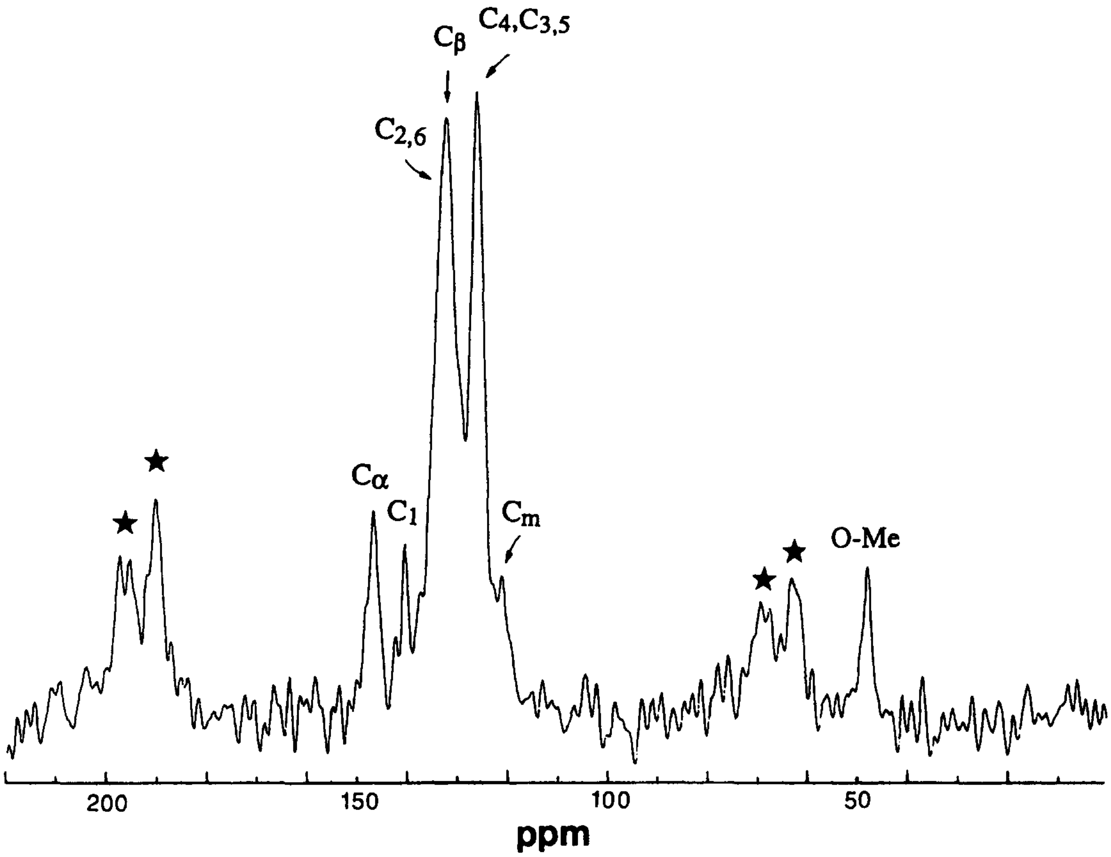


Fig. 3. High-resolution solid-state ^{13}C CP/MAS spectrum of Ge(tpp)(OMe)$_2$ (**2**) at 50.33 MHz with a spinning rate of 3.2 KHz at 24°C. Assignments: singlet at 146.5 ppm, C_α; singlet at 140.2 ppm, C_1; multiplet at 132.3 ppm, $C_{2,6}$ and C_β; multiplet at 128.1 ppm, C_4 and $C_{3,5}$; singlet at 120.9 ppm, C_{meso}; singlet at 47.4 ppm, O—Me. Spinning sidebands are labelled with an asterisk (*).

time t(= several minutes) after dissolution is shown in Fig. 2. It is dominated by the Ge(tpp)$(OH)_2$ resonance (0), with a smaller resonance (*)for Ge(tpp)(OMe)(OH), and the least Ge(tpp)$(OMe)_2$ resonance (Δ). The methanol resulting from the hydrolysis of compounds **2** and **3** shown in stages 1 and 2 is found to be at $\delta = 3.34$ ppm from ^{1}H NMR (shown in Table 1) and 50.7 ppm from ^{13}C NMR measurement (shown in Table 2). At equilibrium, the relative concentrations of **2**, **3** and **4** for Ge(tpp)$(OMe)_2$ (**2**) in CD_2Cl_2 at 24°C are 24, 39 and 37%, respectively. The ratio of $K_1/K_2 = 1.7$ is evaluated for the hydrolysis of compound (**2**) at the same temperature. It is difficult to isolate compound **2** from the above mixture. However, solid-state ^{13}C NMR provides a complementary method for identifying compound **2**. The solid-state ^{13}C CP/MAS spectra of compound **2** at 24°C is shown in Fig. 3 and Table 2. Six major resonances with the α carbon (C_α) at $\delta = 146.5$, C_1 at $\delta = 140.2$, $C_{2,6}$ and C_β at $\delta = 132.3$, C_4 and $C_{3,5}$ at $\delta = 128.1$, *meso* carbon (C_m) at $\delta = 120.9$ and OMe carbon at $\delta = 47.4$ ppm were observed. For comparison, the hydrolysis of Sn(tpp)$(OMe)_2$ and Sn(tptp)$(OMe)_2$ is a two-stage (irreversible) competitive consecutive second-order reaction [5, 6], whereas that of Ge(tpp)$(OMe)_2$ is a two-stage (reversible) equilibrium reaction.

Acknowledgements—Financial support from the National Research Councils of the Republic of China under Grants NSC 86-2113-M-005-008 and NSC 85-2113-M005-001 is gratefully acknowledged.

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